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Constant parameter of hard convex fluid

V S Giri[1*] and B P Akhouri[2]

University Department of Physics, Ranchi University, Ranchi-834 008, Jharkhand, India

[2] Department of Physics, Cambridge Institute of Technology,
Cambridge Village - Tatisilwai, Ranchi-835 103, Jharkhand, India

E-mail : VIGiri@yahoo.com

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Abstract The isotropic-symmetric and orientational co-relations for hard convex bodies (HCB's) model, exhibit simpler behaviour in the surface to surface than in the more customary center-to–center coordinate representation. It is the support function $h(x)$ which defines the analytical properties of this model. The intermolecular potential field has been proposed in terms of the support function. The intermolecular potential for HCB's reduces to hard sphere (HS) intermolecular potential for major and minor axis ratio equal to one and has exactly the same surface-to-surface distribution as for HCB's. The constant parameters of the potential function have been determined empirically by fitting the theoretical virial coefficient with quantum correction to experimental virial coefficient data. The resulting second virial coefficients agree well with the available experimental data.

Keywords Hard convex fluid, support function $h(x)$, virial co-efficient, constant parameters

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The second virial coefficient plays an important role in defining the properties of any kind of fluid model. It is the intermolecular potential field which leads to theoretical values of the second virial coefficient .The second virial coefficient for (hard convex bodies) HCB's model has been expressed by defining the intermolecular attractive and repulsive potential in terms of the support function $h(x)$, which defines the analytical properties . The intermolecular potential has been generalized on the supposition that, it is a function of the shortest distance between the surface-to-surface of the molecules retaining the Lennard-Jones potential characteristics. This expression has been used for calculating the constant parameters for this model of He^4. The purpose of this note is to show that the conditions of accuracy, generality and integrability are satisfied in a very simple manner by using the surface-to-surface HCB's model of intermolecular potential.

The set of coordinates specifying the relative separation and orientation of pair of HCB's involve the minimum surface-to-surface separation K, measured along the common surface normal K and angles measured relative to the surface normal.

*Corresponding Author

The necessary properties of HCB's are summarized by Kihara[1] and others [2,3]. The support function $h(x)$ is defined as the projection

$$h(x) = \hat{K}.\rho, \tag{1}$$

where ρ is the vector extending from the center to the point on the surface to the minimum separation and

$$x = \hat{K}.\hat{e} = \cos\theta, \tag{2}$$

where x defines the orientation of HCB's and the unit vector $\hat{e}$ is the director axis.

The expression for intermolecular pair potential for HCB's model is taken as

$$\varphi(K) = 4E\left[(h(x)/K)^{12} - (h(x)/K)^{6}\right]. \tag{3}$$

For the HCB's with semi-major axis a and semi - minor axis b, the support function is

$$h(x) = b\left[1+\varepsilon.x^2\right]^{1/2}, \tag{4}$$

where $\varepsilon = (a/b)^2 - 1$.

The pair potential for HCB's is now characterized by three constant parameters a, b and E. The potential well minimum occurs at $K = 2^{1/n}\ h(x)$. Also, $\phi(K) = 0$ for $h(x) = K$ and $\phi(K) = \infty$ for $K = 0$. The support function $h(x)$ for $a/b = 1$ reduces to a (or $= b$), and the intermolecular potential for HCB's reduces to hard sphere inter-molecular potential which has exactly the same surface-to-surface distribution as the HCB's [2].

The second virial coefficient in classical statistical mechanics in terms of center-to-center (r,θ,φ) coordinate system may be written as

$$B(T) = N/4 \iiint \left[1 - e^{-\varphi(r)/kT}\right] dr^3. \tag{5}$$

The virial coefficient described for center-to-center (r,θ,φ) coordinate system has been expressed in terms of surface-to-surface (K,θ,φ) coordinate system. The full Jacobian for the transformation from center-to-center to surface-to-surface coordinate system is given in Ref. [3].

$$dr^3 = \left|\partial r/\partial\theta \times \partial r/\partial\varphi . k\right| d\theta d\varphi dK$$

$$= S(x,K)\, d\theta d\varphi dK\ , \tag{6}$$

where θ,φ are the polar and azimuthal angles respectively. The weight function $S(x, K)$ for each value of the surface-to-surface distance K is Jacobian determinant. The *resulting* expression for the classical second virial coefficient has been expressed in a rapidly converging infinite series of Gamma function. The expression is

$$B_{cl} = -C L_{-1} K_3/48 - C\varepsilon/48\left[2L_0/\varepsilon + (L_1 - M_1)\right]K_2$$

$$-C\varepsilon^2/48\left[L_1/\varepsilon^2 + (L_2 - M_2)/\varepsilon\right.$$

$$\left. +1/4(L_3/2 - M_3 + N_3/2)\right]K_1\ , \tag{7}$$

where, $C = N\pi b^3$,

$$L_P = \int (1+\varepsilon.x^2)^{1/2-P} dx,$$

$$M_Q = \int x^2.(1+\varepsilon.x^2)^{1/2-Q} dx\ , \tag{8}$$

$$N_R = \int x^4.\left(1+\varepsilon.x^2\right)^{1/2-R} dx,$$

with $K_n = \sum_{s=0} 1/s!\,(1/\gamma)^{s/2+n/12}\,\Gamma(s/2 - n/12)$,

where $n = 1, 2, 3$. and $\gamma = kT/4E = T^*/4$.

At moderately low temperature the quantum deviations from classical behaviour are small. So the quantum mechanical second virial coefficient may be written as the classical second virial coefficient plus the quantum correction terms. The quantum analogue of eq. (5) has been used for this. The quantum statistical correction can be represented with sufficient accuracy by the two following terms of the expansion down to moderately low temperatures, since the terms involving higher orders would have to be considered in third and higher virial coefficients but do not affect the second virial coefficient [4]. The quantum second virial coefficient assumes the form

$$B = B_{cl} + B_1 + B_2\ , \text{ a term described in the following} \tag{9}$$

where B_1 and B_2 are the quantum correction terms.

We have not taken into account the symmetry characters of the eigen functions which results from the statistics of the particles and are of importance when De Broglie wave length of the molecules is of the order of magnitude of the average distance between the molecules. The expression (9) may be refined by taking the influence of the symmetry requirements into account *i.e.*, for a quantum statistical ideal gas. Therefore, the second virial coefficient becomes

$$B = B_{cl} + B_1 + B_2 + B_{id}\ , \tag{10}$$

where B_{id} is the quantum analogue of eq. (5) for ideal gas and center-to-center (r,θ,φ) coordinate system has been expressed in terms of surface-to-surface (K,θ,φ) coordinate system for ideal gas.

The lower temperature of applicability of eq. (10) is about 40^0K for Helium[5]. We have developed expressions for the numerical computation of B_1, B_2, and B_{id} on the basis of the intermolecular potential given by eq. (3) for HCB's in terms of a rapidly converging infinite series of Gamma-functions[6]. The expression for the first correction term is

$$B_1 = -C\Delta^{*2} L_0 K_1/4 - C\varepsilon\Delta^{*2}/4\left[2L_1/\varepsilon + (L_2 - M_2)\right]K_0$$

$$-C\varepsilon\Delta^{*2}/4\left[L_2/\varepsilon^2 + (L_3 - M_3)/\varepsilon\right.$$

$$\left. +\tfrac{1}{4}(L_4/2 - M_4 + N_4/2)\right]K_{-1} \tag{11}$$

with $K_{n'} = \sum_{S=0}^{\infty}\left[(11n' - 36s)/2304.\pi^2)\right]\left(2^{(s+13/6)}/s!\right)\times$

$$(E/kT)^{(s/2+13/12)}\,\Gamma\left[(6S - n')/12\right],$$

where $n' = -1, 0, 1$.

The expression for second correction term is

$$B_2 = -C\Delta^{*4} L_1 K_{-1}/4 - C\varepsilon\Delta^{*4}/4\left[2L_2/\varepsilon + (L_3 - M_3)\right]K_{-2}$$

$$-C\varepsilon\Delta^{*4}/4\left[L_3/\varepsilon^2+(L_4-M_4)/\varepsilon\right.$$

$$\left.+\tfrac{1}{4}(L_5/2-M_5+N_5/2)\right]K_{-3}, \qquad (12)$$

with $$K_{n''}=\sum_{S=0}^{\infty}\left[(767n''+4728s+3024s)/1474560.\pi^4)\right]\times$$

$$\left(2^{(s+n''/6+4)}/s!\right)\cdot(E/kT)^{(s/2+n''/12+2)}\Gamma\left[(S/2-n''/12)\right],$$

where $n''=-1,-2,-3....$

The ideal gas statistically define as a system of non-localized particles whose potential of interaction is zero for all distances Therefore ,the expression for B_{id} is

$$B_{id}=\pm C\Delta^*/16\,T^{*1/2}\,\pi^{1/2}\left\{\Delta^{*2}/4\pi^2T^*L_{1/2}+\Delta^*/\pi^{3/2}T^{*1/2}\right.$$

$$\times\left[2L_1+\varepsilon(L_2-M_2)\right]+2\left[L_{3/2}-\varepsilon(L_{5/2}-M_{5/2})\right.$$

$$\left.\left.+\varepsilon^2/8(L_{7/2}-2M_{7/2}+N_{7/2})\right]\right\}, \qquad (13)$$

in which negative sign holds for systems with symmetric eigen functions (Bose– Einstein statistics) and the positive sign for systems with anti-symmetric eigen functions (Fermi–Dirac statistics), $\Delta^*=\dfrac{h}{b\sqrt{mE}}$ is the quantum mechanical parameter, m is the mass of He^4, h is the Planck's constant and $T=kT/E$.

The determination of the constant parameters a, b, E and Y have been carried out by a process of successive approximation by using eq. (10). We have obtained the values of a, b and E at 71.5° K from the available experimental data [7] by using only the classical contribution to the second virial coefficient by the method of Lennard- Jones [8]. These values are used in the computation of the first approximation of B_1, B_2 and B_{id} These known quantum corrections have been used for determination of new values of parameters in B_{id}. This process has been repeated till a consistent set of values of parameters are obtained. The values of parameters obtained in this way are tabulated in Table 1. The classical and quantum mechanical theoretical second virial coefficient have been calculated with these known parameters. The behaviour of the second virial coefficient for helium obtained with these parameters are presented together with the experimental data in Figure 1. This represents the quantum deviations of second virial co-efficient also, which depends on the magnitude of the quantity Δ^*. The expansions in powers of Δ^* in eq. (10) converges less rapidly as deviation from classical behaviour becomes greater. The larger the value of Δ^*, the greater the quantum deviations. So eq. (10) may not be used below about 40° K for He. At lower temperatures, the quantum deviations are quite appreciable for helium [9]. The agreement between the theoretical and experimental values is as good as can be expected, for the ratio of major and minor axis equal to 2.

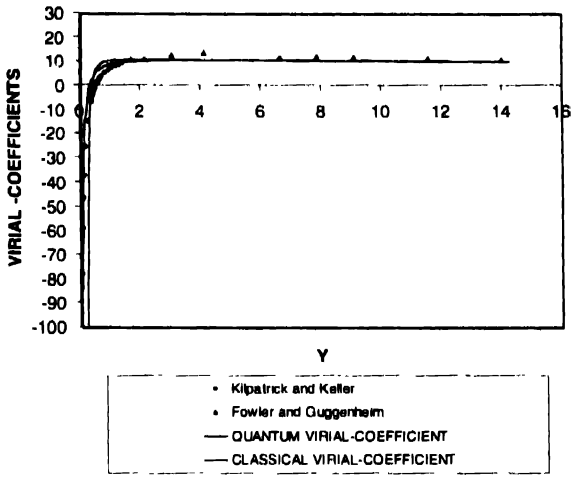

Figure 1. Plot of virial coefficient *versus* Y (see Table 1).

The proposed potential for HCB's in terms of support function simplifies the determination of constant parameters of the HCB model .The quantum mechanical study of the transport properties of the HCB fluid is the solution of radial wave equation for a pair of interacting bodies. This equation may be written in reduced form by using the parameters in the proposed potential as a basis for determination of phase shifts. The values of quantum second virial coefficient computed with these parameters fitted well with the experimental data. So we may safely conclude that the parameters for the potential fit the experimental values of the second virial coefficient of He^4 for the hard convex fluid very well.

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Table 1. Constant parameters of He^4 at ratio a/b = 2.

Y = kT/4E	Major axis(a) in c.m.		Minor axis (b) in cm		Δ_h^*	E (In erg)
	Classical	Quantum	Classical	Quantum	4.921	1.414×10^{-11}
1.749	2.828×10^{-8}	2.792×10^{-8}	1.414×10^{-8}	1.396×10^{-8}		

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